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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

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ATOFINA Research
Zone Industrielle C
7181 Seneffe (Feluy)
BELGIQUE

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Apparatus and method for controlling the injection of catalyst slurry in a polymerization reactor.

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Apparatus and method for controlling the injection of catalyst slurry in a polymerization reactor

Field of the invention

This invention relates to the control of catalyst feeding to a polymerisation reactor. In a first aspect, the invention relates to an apparatus for controlling catalyst feeding to a polymerisation reactor. In another aspect the invention relates to a method for controlling catalyst feeding to a polymerisation reactor. More in particular, the invention relates to an apparatus and a method for controlling the feeding of a metallocene or a chromium catalyst to a polymerisation reactor wherein polyethylene is prepared.

Background

In a typical polymerization reaction, monomer, diluent and a dry particulate catalyst are fed to a reactor where the monomer is polymerized. The diluent does not react but is typically utilized to control solids concentration and also to provide a convenient mechanism for introducing the catalyst into the reactor. The reactor effluent, a mixture of polymer, diluent and unreacted monomer, is removed from the reactor and fed to a flash tank where the polymer is separated from the diluent and unreacted monomer. Typically, catalyst will be contained in the polymer.

Polyethylene (PE) is synthesized via polymerizing ethy lene (CH_2=CH_2) monomer and optionally a higher 1-olefin comonomer such as 1-butene, 1-hexene, 1-octene or 1-decene. Because PE is cheap, safe, stable to most environments and easy to be processed polyethylene polymers are useful in many applications. According to the synthesis methods, PE can be generally classified into several types such as LDPE (Low Density Polyethylene), LLDPE (Linear Low Density Polyethylene), and HDPE (High Density Polyethylene). Each type of polyethylene has different properties and characteristics.

The use of metallocene catalysts in the production of polyolefins in general, and of polyethylene in particular, is known in the art.

In general, for preparing catalyst slurry, a mixture of dry solid particulate catalyst and diluent are apportioned in a catalyst storage vessel for thorough mixing. Then such catalyst slurry is typically transferred directly to a polymerization reaction vessel for contact with the monomer

reactants, generally under high pressure conditions. However, it is important to control catalyst flow to a reactor since unexpected or uncontrolled catalyst injection in a reactor could lead to runaway reactions. Direct feeding of catalyst slurry from a storage vessel to a reactor has the disadvantage that the feeding rat e of the catalyst to the reactor cannot be adequately controlled. Also, in cases involving direct feeding of a catalyst from a mud pot to a reactor, the metallocene catalyst can be completely flushed in the reactor, when a problem occurs during the preparation of the metallocene catalyst. Such uncontrolled catalyst feeding may induce runaway reactions in the reactor.

Improvements in the feeding of catalyst to a reactor have been described, e.g. in US 5,098,667. This US patent describes a method for feeding of a catalyst in general to a reactor comprising preparing heavy slurry in a storage vessel, and then transferring the heavy slurry to a mixing vessel, where the heavy slurry is diluted and subsequently transferred to a reactor. In the described method th e flow rate of the dilute slurry is manipulated so as to provide a desired flow rate of solid particles contained in the dilute slurry. Continuous catalyst flow is maintained at a desired rate in response to a computed value of the mass flow rate of the solid catalyst particles contained in the dilute slurry. The computed mass flow rate of catalyst particles is based upon "on line" measurements of density and flow rate of the dilute catalyst slurry stream flowing to the reactor, and on predetermined densiti es of the solid catalyst particles and the liquid diluent constituting the slurry. However, although the method provides an improvement on the control of catalyst flow, it has the disadvantage that the catalyst flow rate is not adjusted in function of the reaction conditions in the polymerization reactor.

Therefore, there remains a need in the art for providing an improved method for controlling catalyst feeding, and in particular feeding of metallocene or chromium catalysts, to a polymerization reactor.

Furthermore, metallocene catalysts are usually employed with a co -catalyst for olefin polymerization, which can significantly enhance the polymerization efficiencies to beyond a million units of polymer per unit of catalyst. The co-catalyst is an organom etallic compound, or a mixture of non-coordinated Lewis acid and alkylaluminium as it is well known in the art. A number of techniques for the introduction of the co -catalyst to a polymerization reactor has been proposed. For instance some techniques consi st of introducing the co -catalyst directly

into the polymerization reactor. However, such technique does not allow bringing the co -catalyst into contact with the metallocene catalyst before entering the reactor, although such pre-contact is particularly de sirable in order to provide effective catalyst -co-catalyst mixtures. Another technique consists of contacting the catalyst and co -catalyst before their introduction into the polymerization medium. In this latter case, however, having regard to the fact tha t the catalyst systems employed usually have maximum activity at the commencement of polymerization, it may be difficult to avoid reaction runaways liable to involve the formation of hot spots and of agglomerates of molten polymer.

In view hereof, it can be concluded that there remains also a need in the art for providing an improved method for controlling catalyst feeding, in particular feeding of metallocene catalysts, in pre-contact with a co-catalyst, to a polymerization reactor.

It is therefore a gen eral object of the present invention to provide an improved apparatus and method for feeding catalyst to a polymerization reactor, at a controlled flow rate. Another object of the present invention is to provide an apparatus and method for controlling the injection of catalyst slurry, in particular metallocene or chromium catalyst slurry, in a polymerisation reactor, wherein polyethylene is prepared.

It is a further object of the present invention to provide an apparatus and method for controlling catalyst feeding, and in particular feeding of a metallocene catalyst, being in pre -contact with a co-catalyst, to a polymerisation reactor, wherein polyethylene is prepared.

Furthermore, the present invention aims to provide a method for improved control of the polymerization reaction of ethylene in a reactor.

Summary of the invention

In accordance with the present invention, an apparatus and a method are provided for controlling the injection of catalyst slurry into a polymerization reactor wherein polyethylene is prepared. Said catalyst slurry consists of solid catalyst in a hydrocarbon diluent.

In a first aspect, the invention relates to an apparatus for controlling the injection of catalyst slurry in a polymerization reactor comprising

- one or more storage vessels for storing catalyst slurry consisting of solid catalyst in a hydrocarbon diluent, whereby each vessel is provided with means for transferring said catalyst slurry from said storage vessels to a mixing vessel,
- a mixing vessel, being connected wi th said storage vessels by means of said transferring means, for diluting said catalyst slurry to a suitable concentration for use in a polymerisation reaction, and
- one or more conduits, connecting said mixing vessel to a polymerization reactor for transferring said diluted catalyst slurry from said mixing vessel to said reactor, whereby each conduit is provided with a pumping means for pumping said slurry to said reactor.

According to the present invention, the catalyst is not introduced directly from th e storage vessels to the reactor. The apparatus further comprises a mixing vessel, which acts as a "buffer" between the storage vessels and the reactor. The mixing vessel is operated at a pressure lower than the reactor pressure, thus eliminating the risk of uncontrolled high catalyst injection under high pressure to the reactor. Furthermore, such mixing vessel enables to dampen the discontinuous catalyst feed fluctuations to the reactor. Another advantage of providing a mixing vessel is that catalyst slurr y can be further diluted to a concentration suitable for use in the polymerization reactor and that a slurry having a desired, substantially constant, concentration can be prepared. Moreover, a suitable, relatively low, concentration of catalyst, preferabl y comprised between 0.1 and 10 % by weight, more preferably between 0.1 and 4 %, even more preferred between 0.1 and 1 % and most preferred 0.5 % by weight, will enable to use membrane pumps for injecting the catalyst slurry in the reactor.

The use of membrane pumps in the present apparatus permits to transfer catalyst slurry to said reactor at controllable catalyst flow rate. In addition, t he membrane pumps are particularly suitable for adjusting catalyst flow rate to a suitable value which is in accorda nce with the polymerization reaction taking place in the reactor , since these pumps are controllable in function of the concentration of a reactant in said reactor.

In another aspect, the present invention relates to a method for controlling the injectio n of catalyst slurry into a polymerization reactor comprising the subsequent steps of:

a) providing solid catalyst and a hydrocarbon diluent in one or more storage vessels such that a catalyst slurry is obtained in said vessel,

b) transferring said catalyst slu rry from said storage vessel to a mixing vessel wherein said catalyst slurry is diluted for obtaining a suitable concentration for use in a polymerisation reaction,

c) pumping said diluted catalyst slurry at a controlled flow rate from said mixing vessel to said polymerisation reactor through one or more conduits, by means of a pumping means, provided in each of said conduits.

The present method provides improved injection of catalyst slurry at a suitable, controlled and limited flow rate in a polymerization reactor. Therefore, according to the present method, catalyst slurry is first transferred to a mixing vessel, where it is kept at a suitable concentration, before it is injected in the reactor. The method does not involve direct injection of catalyst from a storage vessel to a reactor.

In addition, pumping means, preferably membrane pumps, are provided in each conduit for transferring the catalyst slurry from the mixing vessel to the polymerisation reactor. These pumps assure the transfer of catalyst slu rry to said reactor at controllable flow rate. Moreover, the membrane pumps are capable of being regulated to adjust catalyst flow to said reactor in function of the polymerisation reaction in said reactor, since these pumps are controllable and adjustable in function of a reactant concentration in the reactor.

According to the invention the present apparatus and method enable to feed a reactor with an optimal concentration of catalyst slurry at a suitable catalyst flow rate, and as a consequence thereof enable to considerably improve the productivity in the polymerisation reaction in the reactor.

The present invention is in particular suitable for controlling the injection of metallocene catalyst slurry or chromium catalyst slurry in a polymerization r eactor wherein polyethylene is prepared.

The various features which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this disclosure. For a better understanding of the invention, its operating ad vantages and specific objects attained by its uses, reference is

made to the accompanying drawings and descriptive matter in which preferred embodiments of the invention are illustrated.

Detailed description of the drawings

Figure 1 is a schematic repres entation of a preferred embodiment of an apparatus according to the invention for controlling the injection of catalyst in a polymerisation reactor.

Figure 2 is a detailed representation of a preferred embodiment of a metering valve, used in the apparatus according to the present invention for controlling the transfer of catalyst slurry from a storage vessel to a mixing vessel.

Figure 3 is a schematic representation of a single loop polymerization reactor.

Figure 4 is a schematic representation of a dou ble loop polymerization reactor.

Detailed description of the invention

The present invention is described in terms of controlling the feeding of catalyst slurry to a polymerization reactor, in particular to a polymerisation reactor wherein polyethylene (PE) is prepared. Polymerization of ethylene may for instance be carried out in loop reactors. In such polymerization reactions, e thylene, a co-monomer such as hexene-1, a light hydrocarbon diluent such as isobutane, a catalyst and hydrogen are fed to a r eactor. In a particularly preferred embodiment, the invention relates to a process of controlling the feeding of catalyst slurry to a polymerisation reactor wherein bimodal polyethylene is prepared. "Bimodal PE" refers to PE that is manufactured using two reactors, which are connected to each other in series. However, the present method for controlling catalyst feeding to a polymerisation reactor should be understood to be applicable to reactors wherein other types of polymerisation reactions can take place as well.

According to the present invention the term "catalyst" is defined herein as a substance that causes a change in the rate of a polymerization reaction without itself being consumed in the reaction. According to a preferred embodiment said catalys t is a metallocene or chromium catalyst. According to another embodiment, said catalyst may also be a Ziegler-Natta catalyst. In another particularly preferred embodiment, said catalyst may comprise any catalyst which is provided on a Si support.

The metallocene catalysts are compounds of Group IV transition metals of the Periodic Table such as titanium, zirconium, hafnium, etc., and have a coordinated structure with a metal

compound and ligands composed of one or two groups of cyclopentadienyl, indenyl, fluorenyl or their derivatives. Use of metallocene catalysts in the polymerization of olefins has various advantages. Metallocene catalysts have high activities and are capable of preparing polymers with enhanced physical properties in comparison with the polymers prepared using Ziegler-Natta catalysts. The key to metallocenes is the structure of the complex. The structure and geometry of the metallocene can be varied to adapt to the specific need of the producer depending on the desired polymer. Metallocen es comprise a single metal site, which allows for more control of branching and molecular weight distribution of the polymer. Monomers are inserted between the metal and the growing chain of polymer.

The term "metallocene catalyst" is used herein to des cribe any transition metal complexes consisting of metal atoms bonded to one or more ligands. In a preferred embodiment, the metallocene catalyst has a general formula MX, wherein M is a transition metal compound selected from group IV and wherein X is a ligand composed of one or two groups of cyclopentadienyl (Cp), indenyl, fluorenyl or their derivatives. Illustrative examples of metallocene catalyst s comprise but are not limited to Cp_2ZrCl_2, Cp_2TiCl_2 or Cp_2HfCl_2.

The metallocene catalysts generally are provided on a solid support. The support should be an inert solid, which is chemically unreactive with any of the components of the conventional metallocene catalyst. The support is preferably a silica compound.

The term "chromium catalysts" refers to ca talysts obtained by deposition of chromium oxyde on a support, e.g. a silica or aluminum support. Illustrative examples of chromium catalyst s comprise but are not limited to $CrSiO_2$ or $CrAl_2O_3$.

The term "Ziegler-Natta catalyst" refers to a catalyst of the general formula MX_n wherein M is a transition metal compound selected from group IV to VII, wherein X is a halogen, and wherein n is the valence of the metal . Preferably, M is a group IV, group V or group VI metal, more preferably titanium, chromium or vanadium and most preferably titanium. Preferably, R is chlorine or bromine, and most preferably, chlorine. Illustrative examples of the transition metal compounds comprise but are not limited to $TiCl_3$, $TiCl_4$. In a particularly preferred embodiment of the in vention said catalyst is a titanium tetrachloride ($TiCl_4$) catalyst.

Ziegler-Natta catalysts generally are provided on a support, i.e. deposited on a solid support. The support should be an inert solid, which is chemically unreactive with any of the components of the conventional Ziegler -Natta catalyst. The support is preferably a silica or magnesium compound. Examples of the magnesium compounds which are to be used to provide a support source for the catalyst component are magnesium halides, dialkoxymagnesiums, alkoxymagnesium halides, magnesium oxyhalides, dialkylmagnesiums, magnesium oxide, magnesium hydroxide, and carboxylates of magnesium.

The term "co-catalyst" as used herein is defined as a catalyst that can be used in conjunction with another catalyst in order to improve the activity and the availability of the other catalyst in a polymerisation reaction. In a preferred embodiment, said co -catalyst is a catalyst suitable for being used in conjunction with a metallocene catalyst. Such co -catalysts may include organometallic compounds, or a mixture of non -coordinated Lewis acids and alkylaluminiums as it is well known in the art.

Preferably, organometallic compounds of periodic groups I to III are used as co -catalyst according to the present invention. In a particularly preferred embodiment, said co -catalyst is a catalyst suitable for being used in conjunction with a metallocene catalyst and is an organoaluminium compound, being optionally halogenated, having general formula AlR_3 or AlR_2Y, wherein R is an alkyl having 1 -16 carbon atoms and R may be the same or different and wherein Y is hydrogen or a halogen. Examples of co -catalysts comprise but are not limited to trimethyl aluminum, triethyl aluminum, di -isobutyl aluminum hydride, tri-isobutyl aluminium, tri-hexyl aluminum, diethyl aluminum chloride, or diethyl aluminum ethoxide, A particularly preferred co -catalyst for use in the present invention is tri -isobutyl aluminium.

The invention will be described hereunder with reference to the control of feeding of a metallocene catalyst supported on silica impregnated by methylaluminoxane (MAO), to a polymerisation reactor wherein ethylene is polymerised. In a preferred embodiment, isobutane is used as diluent for the metallocene catalyst. As co -catalyst for the metallocene catalyst, reference is made to a tri -isobutyl aluminium co -catalyst, referred to as TIBAL herein. However, it should be understood that the present device is applicable to other types of catalysts, such as for instance chromium catalyst s, and to other types of co -catalysts as well.

For reasons of brevity and clarity, conventional auxiliary equipment such as pumps, additional valves, and other process equipment have not been included in this description and the accompanying drawings as they play no part in the explanation of the invention. Also additional measurement and control devices which would typically be used on a polymerization process have not been illustrated.

Referring now to FIG. 1, an apparatus according to the present invention is illustrated. The apparatus comprises one or more catalyst storage vessels, or so-called mud tank or pot 2 which contain solid-liquid slurry of metallocene catalyst and isobutane diluent. The slurry is fed from the mud pot 2 through the combination of conduit 6, 7 and conduit 15 to a mixing vessel 3, wherein the slurry is diluted to a suitable concentration. In addition, the apparatus further comprises one or more conduits 4 which connect the mixing vessel 3 to a polymerization reactor 1 and through which the diluted catalyst slurry is pumped from said mixing vessel 3 to the reactor 1, by means of pumping means 5 provided in these conduits 4.

The metallocene catalysts can be provided under a dry form in commercially available drums or tote bins 26. In general such drums containing dry catalyst powder are not able to handle high pressures. For instance, the pressure in such drum may comprise approximately between 1.1 and 1.5 bar, and preferably 1.3 bar. Depending on the diluent used, it may be required to bring the catalyst under higher pressure conditions in the storage vessel 2. Using appropriate systems, the catalyst is therefore preferably transferred from such drums to a storage vessel 2, which is suitable for handling higher pressures, if this is required by the diluent. This is for instance the case when isobutane is used, since this diluent is only liquid at higher pressure levels. In case for instance hexane is used as diluent, storage vessel 2 is not required, since this diluent is liquid at low pressures. According to a preferred embodiment, the metallocene catalyst is provided from drums 26 to a storage vessel 2 through a conduit 27, preferably by means of nitrogen pneumatic transfer or by gravity. However, it is clear that also other types of catalyst feeding to the storage vessel are suitable and fall within the scope of the present invention. In an alternative embodiment, the metallocene catalyst can also be provided in a commercial container that is suitable for handling higher pressure comprised between 7 and 16 bar. In such case such commercial container is considered as a storage vessel 2 and the catalyst can be fed directly from this commercial container to a mixing vessel 3. Isobutane diluent is brought into the storage vessel 2 by means of a control valve.

In the storage vessel, the metallocene catalyst is stored under liquid olefin free isobutane pressure, preferably comprised between 7 and 16 bar. The pressure in the storage vessel is preferably lower than the pressure in the reacto r, in order to avoid leakage of catalyst from the storage vessel to the reactor. Catalyst settles in storage vessel 2, since no agitation means are provided in this vessel.

The catalyst is subsequently transferred by means of transferring means from the storage vessels 2 to a mixing vessel 3 wherein said catalyst is diluted for obtaining a suitable concentration for use in a polymerisation reaction. Preferably the catalyst mixtures in the storage vessel 2 which contain proportionally high amounts of solid s are fed to the mixing vessel 3 through conduits 6, 7. As represented, two storage vessels are connected with two different conduits 6, 7 to a common mixing vessel 3. In such case, the catalyst mixtures in conduits 6, 7 are preferably discharged in a comm on conduit 15, before being supplied to the mixing vessel 3. However, according to the invention, also only one storage vessel 2 may be provided. To avoid remaining catalyst in storage vessel 2, the vessel is flushed with isobutane, such that remaining cat alyst is transferred to the mixing vessel 3.

In a particularly preferred embodiment, the conduits 6, 7 are interconnected by means of connecting lines 8. Such lines 8 enable that the different storage vessels 2 can be used in accordance with all provided conduits 6, 7. For instance, as represented in FIG. 1, in case two storage vessels 2 are provided, each having a conduit 6 or 7, the conduit 6 for transferring said catalyst from a first storage vessel 2 to a mixing vessel 3 is interchangeable with a second conduit 7 for transferring said catalyst from a second storage vessel 2 to a mixing vessel 3 through lines 8 connecting said first 6 with said second 7 conduit. Such interconnection permits, in case of interruption of catalyst transfer through one condu it 6, to discharge the catalyst to the mixing vessel 3 through a second conduit 7.

Each conduit 6, 7 is preferably equipped with metering valves 9 allowing the feeding of a controlled flow rate of catalyst to the mixing vessel 3. These valves are preferab ly provided downstream the connecting lines 8. The pressure difference between the storage vessel 2 and the mixing vessel 3 supplies the motive force to feed the catalyst to the mixing vessel.

The metering valves 9 allow the transfer of a predetermined v olume of catalyst to the mixing vessel 3. The catalyst slurry discharged by the valves is carried to the mixing vessel by an

isobutane flow. Therefore, the conduits 6, 7, each are preferably further provided with a port 24, which can be connected for flush ing with diluent. Said port is preferably provided downstream the valves 9.

In a preferred embodiment, the metering valves 9 are ball check feeder or shot feeder valves. FIG. 2 illustrates a ball check feeder valve arrangement suitable for utilization in the present apparatus. However, it is clear that other types of valves could be used as well in accordance to the present invention. Referring to Fig. 2, a preferred embodiment of a valve is represented which includes a body 16, having an inlet 17 and an outlet 18, a member 19, containing a metering chamber 20, which is rotatable within the body 16 for communicating with the inlet 17 and outlet 18 in at least two positions, a ball shaped piston 21, which moves with a reciprocating motion within the chamber 20 as the member 20 is rotated. The working mechanism of such valve involves a sequence of charging, valve actuation and dumping of a specific volume of catalyst slurry from a storage vessel 2 to a mixing vessel 3. During operation, when the valve takes a first position, a fixed quantity of concentrated slurry flows through the inlet 17 and fills a chamber 20 within the valve 9. Said quantity is released to the mixing vessel 3 when the valve is actuated to a second position. The valve 9 thus delivers a fixed volume of concentrated slurry from storage vessel 2.

More in detail the mechanism of action of this special ball check valve 9 is the following. The valve 9 is charged or filled with a predetermined volume of a mixture of catalyst and diluent when in a first position. Periodically this ball check valve is actuated to a second position and this volume of the mixture is dumped from the valve into the mixing vessel 3. The ball check valve 9 is then recharged or refilled with the predetermined volume of th e mixture in preparation for actuation back to the first position where the second volume of mixture is dumped from the valve 9 into the mixing vessel 3. Concentrated slurry flow from storage vessel 2 to the mixing vessel 3 is thus accomplished by the cycl ic operation of the metering valve 9. The cycle time of the valves determines the catalyst flow rate to the mixing vessel 3. For instance, when this cycle time is increased, the flow rate of catalyst decreases.

Due to the high degree of dilution and the use of membrane pumps the catalyst feeding system from the storage vessel 2 to the mixing vessel 3 advantageously allows providing catalyst at a controlled flow rate to the mixing vessel 3. In addition, the feeding system permits to keep the concentration of catalyst slurry in the mixing vessel 3 at a substantially

constant level, since catalyst flow regulated by the valve 9 to the mixing vessel 3 is dependent on the dosed amount (concentration) of catalyst and diluent in the mixing vessel 3. In a preferred embodiment of the invention the concentration of catalyst slurry in the mixing vessel is kept at a substantially constant level. According to the invention the ratio between diluent and catalyst is adequately controlled. This is enabled by adequate control of catalyst feeding from the storage vessel by means of the catalyst feeding system and metering valves 9, and by release of a suitable amount of isobutane to the mixing vessel.

Catalyst wastes can be sent to one or more dump vessels 28, which are preferably provided with stirring means 25 and contain mineral oil for neutralization and elimination of the wastes. The dump vessels are preferably connected by means of conduits 29 to the catalyst feeding conduits 6 or 7, upstream of the metering valves 9. The dump vessel 28 is preferably also connected to the mixing vessel 3, for transferring catalyst wastes by means of a conduit 23. The dump is provided with a heated vessel, e.g. steam jacket, where the isobutane is evaporated and sent to distillation or to the flare. In order to avoid the transfer of catalyst fragments when transferring the evaporated isobutane, guard filters are provided with the dump vessels 28. The dump vessels 28 are also provided with pressure controlling means for controlling the pressure in said vessels. The catalyst waste remaining after evaporation of the diluent is removed from the vessels 28, preferably by means of a draining system, provided at the bottom of the vessel 28, and the removed waste is discharged into drums and further destroyed.

According to the present invention, the metallocene catalyst is transferred from the storage vessels 2 to a mixing vessel 3. A stream of isobutane is provided to mixing vessel 3 through a valve which is operably located in conduits 6 and 7. An additional function of this stream is to dillute the concentrated slurry. The mixing vessel 3 can be operated either when full of liquid or not. Preferably, the mixing vessel 3 is operated full of liquid, since if there is an interphase with nitrogen the catalyst slurry might settle or stick to the walls in the vessel.

Preferably, the metallocene catalyst slurry is diluted in a hydrocarbon diluent in the mixing vessel 3 to a concentration between 0.1 % and 10 % by weight. More preferably the slurry is diluted in a hydrocarbon diluent to a concentration comprised between 0.1 % and 4 % by weight, more preferred between 0.1 and 1 %, and even more preferred of 0.5 % by weight. Preparing diluted slurry having these concentrations advantageously enables the further use

of membrane pumps 5 for injecting the slurry in the reactor 1, as described into more detail below. The mixing vessel 3 is also provided with a stirrer 25 for maintaining the homogeneity of the slurry.

Dilute catalyst slurry is withdrawn from the mixing vessel 3 through one or more conduits 4 and provided through these conduits to a polymerization reactor 1. Each conduit 4 is provided with a pumping means 5, which controls the transfer and injection of the metallocene catalyst slurry into the reactors 1. In a particularly preferred embodiment, said pumping means are membrane pumps. The conduits 4 preferably leave the mixing vessel 3 in upward direction under an angle preferably superior to 10°, and more preferably superior to 30°. In addition, the conduit provided downwards the pumping means 5 conducts the catalyst slurry preferably downwardly, under an angle preferably superior to 10°. Such configuration improves the action of the pumping means 5 and also enables to avoid plugging in the pumping means 5 since under this configuration the slurry tends to settle away from the pumps 5 in case the pumps 5 are interrupted or stopped. However, it is to be understood that conducts which extend downwardly are not required if sufficient flushing of the co nduit 4 can be obtained.

The conduits 4 are further provided with isobutane flushing means, either at the inlet 30, at the outlet 33 or at both sides of the membrane pumps 5, as illustrated on FIG. 1. Isobutane flushing means 30, 33 enable to flush isob utane through the conduit 4 and to keep the conduits 4 and the pumping means 5 unplugged. Preferably, there is continuous flushing of the conduit 4 downstream the membrane pump 5 to the reactor 1 by means of isobutane flushing means 33. The conduit 4 upstr eam the pump 5 may be flushed discontinuously, by means of isobutane flushing means 30. When different conduits 4 are provided for connecting the mixing vessel 3 to the reactor 1, generally, one conduit having one active pumping means 5 will be operative, while the other conduits 4 and pumping means 5 will not be operative but will be kept in stand by mode. In this latter case, the conduit 4 downstream the pump 5 will preferably be flushed with a suitable stream of diluent. The conduit 4 upstream the pump 5 may be discontinuously flushed. In addition, two-way valves 31 can be installed on the conduits 4, in order to never stop the pumping means 5.

It is important to correctly control the metallocene catalyst flow rate to the reactor and to pump catalyst s lurry into the reactor at a controlled and limited flow rate. An unexpected flow rate to the reactor could lead to a runaway reaction. A fluctuating flow to the reactor could

lead to reduced efficiency and fluctuations in product quality. Therefore, in a particularly preferred embodiment, the injection pump 5 flow rates are controlled by the reactor 1 activity. The pumping means are in particular controllable in function of the concentration of a reactant in said reactor. Preferably said reactant is the co ncentration of monomer, i.e. ethylene, in the reactor. However, it should be clear that the membrane pumps are controllable in function of the concentration of other reactants, such as e.g. the co -monomer or hydrogen concentrations in the reactor as well. By the use of membrane pumps 5 the invention provides for a good control catalyst flow. In particular, the metallocene catalyst flow rate to the reactors is controlled by adjusting the stroke and/or frequency of the membrane pumps. Furthermore, the pump fl ow rates are controlled by the ethylene concentration in the reactor. In case the ethylene concentration is high in the reactor, more catalyst will be added to the reactor and vice versa. In this way, the variations in ethylene polymerisation rate are take n into account and actual production rate and product properties do not fluctuate significantly. Variations in ethylene polymerisation rate are taken into account and polymerisation reactions under optimal catalyst feeding conditions can be obtained.

In a further embodiment, the present device is further provided with a co-catalyst feeding system, for bringing a co-catalyst into contact with said catalyst slurry before feeding said catalyst slurry to said reactor. A tri -isobutyl aluminium (TIBAL) is prefe rably used as co-catalyst.

The co-catalyst distribution system 11 may comprise two co -catalyst storage vessels wherein co-catalyst is prepared and stored. One vessel may be in connection to the conduit 4 for providing co-catalyst thereto.

Co-catalysts are generally provided in commercial drums. In a storage vessel of the co -catalyst distribution system 11, the TIBAL co-catalyst is generally provided in a solution of hexane or heptane, but can be provided in pure form too. The TIBAL co -catalyst is transferred from the storage vessel through a co -catalyst injection conduit 12, in the conduit 4, which connects the mixing vessel 3 with the reactor 1. Conduit 12 intersects conduit 4, downstream the diaphragm pumps 5 and upstream the reactor 1. In case a flow me asuring means 10 is further provided on the conduits 4, the co -catalyst feeding conduit 12 preferably intersects the conduit 4, downstream of said flow meter 10.

In case the TIBAL co-catalyst is injected in the conduit 4, the injection point is at a distance from the reactor allowing a certain pre-contact time with the catalyst before being supplied to the reactor. In order to have a sufficient pre-contact time, preferably between 5 seconds and 1 minute, between the metallocene catalyst slurry and the TIBAL co-catalyst, small contact vessels 13 are installed on the conduits 4, downstream the injection point of the co-catalyst feeding system. These contact vessels 13 can be agitated or not. In another preferred embodiment, the conduits 4 have an inner diameter comprised between 0.3 and 2 cm, and preferably comprised between 0.6 and 1cm while the diameter of the contact vessels 13 is preferably comprised between 1 and 15 cm and preferably between 6 and 9 cm.

Catalyst wastes can be sent to a dump vessel 28, which is preferably provided with stirring means 25 and contains mineral oil for neutralization and elimination. The dump is provided with a heated vessel, e.g. steam jacket, where the isobutane is evaporated and sent to distillation or to the flare.

In addition, the invention provides an apparatus having conduits 4 which are further provided with measuring means 10, for easily measuring the catalyst flow rate in the conduits 4. These flow measuring means 10 preferably are Coriolis flow measuring means. The means 10 can be provided between the mixing vessel 3 and the membrane pumps 5 or downstream from said pumping means 5. The slurry is preferably injected in ratio control of isobutane diluent to catalyst. The Coriolis meters 10 can measure the flow and the density of the catalyst slurry at the exit of the mixing vessel 3 and indirectly determine the suspended solids concentration. A correlation exists for estimating the concentration of suspended solids based on the slurry density, the carrier fluid density and the solid particle density.

In another embodiment, the catalyst slurry is injected under controlled flow into the reactor. The conduits 4 for transferring catalyst slurry into to the reactor are equipped by one or more valves, preferably piston valves 22. The piston valves 22 are capable of sealing the orifice by which the conduit 4 is connected to the reactor 1. When using different conduits 8 for transferring catalyst slurry to one reactor, only in one conduit 8 the pumping means actively pump catalyst slurry to the reactor, while in other conduits 8 the pumps are not active and the conduits are preferably flushed by isobutane.

In another preferred embodiment, by operation in accordance with the present invention, all lines, vessels, pumps, valves , etc.. can be kept free of clogging by means of flushing or purging with nitrogen or diluent, i.e. isobutane. It is to be understood that where necessary flushing and purging means and lines are available on the device according to the invention in order to avoid plugging, or blocking.

It is clear from the present description that numbers and dimensions of the different parts of the apparatus according to the invention relate to the size of the polymerization reactors and can be changed in function of the reactor sizes.

It is to be understood from the present invention that all indicated pressures values are preferred pressure values, which in general can deviate from the indicated pressure values with approximately $\pm$ 1 bar. It will be evident from the pr esent description that all indicated pressure values in the vessels, conduits, etc.. are values that are lower than the pressure value in the polymerisation reactor.

In another preferred embodiment, it is to be understood that all lines or conduits appli ed in accordance with the present invention may be provided, where necessary with flow measuring means.

In a preferred embodiment, the apparatus according to the invention can be used in a single loop reactor as depicted on FIG. 3 or in a double loop reac tor, as depicted on FIG. 4.

FIG. 3 represents a single loop reactor 100, consisting of a plurality of interconnected pipes 104. The vertical sections of the pipe segments 104 are preferably provided with heat jackets 105. Polymerization heat can be extra cted by means of cooling water circulating in these jackets of the reactor. Reactants are introduced into the reactor 100 by line 107. Catalyst, optionally in conjunction with a co -catalyst or activation agent, is injected in the reactor 100 by means of th e conduct 106. The polymerization slurry is directionally circulated throughout the loop reactor 100 as illustrated by the arrows 108 by one or more pumps, such as axial flow pump 101. The pump may be powered by an electric motor 102. As used herein the t erm "pump" includes any device from compressing driving, raising the pressure of a fluid, by means for example of a piston or set of rotating impellers 103. The reactor 100 is further provided with one or more settling legs 109 connected to the pipes 104 o f the reactor 100.

The settling legs 109 are preferably provided with an isolation valve 110. These valves 110 are open under normal conditions and can be closed for example to isolate a settling leg from operation. Further the settling legs can be provide d with product take off or discharge valves 111. The discharge valve 111 may be any type of valve, which can permit continuous or periodical discharge of polymer slurry, when it is fully open. Polymer slurry settled in the settling legs 109 may be removed by means of one or more product recovery lines 113, e.g. to a product recovery zone.

FIG. 4 represents a double loop reactor 100/116, comprising two single loop reactors 100 and 116, which are interconnected in series. Both reactors 100, 116 consist of a plurality of interconnected pipes 104. The vertical sections of the pipe segments 104 are preferably provided with heat jackets 105. Reactants are introduced into the reactors 100 by line 107. Catalyst, optionally in conjunction with a co -catalyst or activation agent, is injected in the reactor 100 or 116 by means of the conduct 106. The polymerization slurry is directionally circulated throughout the loop reactors 100, 116 as illustrated by the arrows 108 by one or more pumps, such as axial flow pump 101 . The pumps may be powered by an electric motor 102. The pumps may be provided with a set of rotating impellers 103. The reactors 100, 116 are further provided with one or more settling legs 109 connected to the pipes 104 of the reactors 100, 116. The sett ling legs 109 are preferably provided with an isolation valve 110. Further the settling legs can be provided with product take off or discharge valves 111. Downstream the valve 111 at the exit of the settling leg 109 of reactor 100, a three -way valve 114 is provided which allows to transfer polymer slurry settled in the settling legs 109 to the other reactor 116, by means of the transfer line 112. The transfer line 112 connects the three - way valve 114, provided at the exit of the settling leg 109 of one rea ctor 100, with the entry in the other reactor 116, where preferably a piston valve 115 is provided. Polymer slurry settled in the settling legs 109 of reactor 116 can be removed by means of one or more product recovery lines 113, e.g. to a product recovery zone.

The apparatus according to the invention can be applied for feeding a polymerisation reactor. In a preferred embodiment the apparatus is applied for feeding a polymerisation reactor consisting of two liquid full loop reactors, comprising a first an d a second reactor connected in series by one or more settling legs of the first reactor connected for discharge of slurry from the first reactor to said second reactor. Such in series connected reactors are particularly suitable for the preparation of bim odal polyethylene. The present apparatus can be applied

for both reactors. The number of conduits 4 can be divided between the first and the second reactor. It is also possible to use two catalyst preparation and injection apparatuses e.g. when two different catalysts are used.

At the start of the operation of the apparatus, the following subsequent steps are performed. First, the mixing vessel 3 and the conduits provided under the valves 9 are filled with the diluent isobutane. Then, the storage vessels and the conduits 6 and connecting lines 8, provided upstream the valves 9, are supplied with isobutane. Subsequently, the valves 9 are shortly brought into operation, where after the flushing to the reactor 1 is opened and catalyst is injected through cond uits 4 in the reactor.

In another embodiment, the present invention relates to a method for controlling the injection of catalyst slurry in a polymerization reactor 1 wherein polyethylene is prepared, said catalyst consisting of solid catalyst, preferabl y a metallocene catalyst defined as described above in a hydrocarbon diluent, preferably isobutane. However, it is clear that the present method is also suitable for controlling the injection of chromium catalyst slurry in a polymerization reactor 1. The method comprises the subsequent steps of: a) providing solid catalyst and a hydrocarbon diluent in one or more storage vessels 2 such that a catalyst slurry is obtained in said vessel 2, b) transferring said catalyst slurry from said storage vessel 2 to a m ixing vessel 3 wherein said catalyst slurry is diluted for obtaining a suitable concentration for use in a polymerisation reaction, and c) pumping said diluted catalyst slurry at a controlled flow rate from said mixing vessel 3 to said polymerisation react or 1 through one or more conduits 4, by means of a pumping means 5, provided in each of said conduits 4.

According to a preferred embodiment, the method comprises transferring said catalyst slurry from a storage vessel 2 to a mixing vessel 3 at a controll ed flow rate, by controlling the ratio between diluent and catalyst in the mixing vessel 3 . Control of the flow rate is enabled by providing a catalyst feeding system for feeding catalyst slurry from the storage vessel 2 to the mixing vessel 3, which compr ises a conduit 6, 7, connected to said vessel 2 and metering valves 9, preferably ball check feeder or shot feeder valves , on said conduit 6, 7. The catalyst flow from the storage vessel 2 to the mixing vessel 3 is regulated by the valves 9 and is dependent on the dosed amount (concentration) of catalyst and diluent in the mixing vessel 3. The ratio between diluent and catalyst is adequately controlled. This is enabled by adequate control of catalyst supply from the storage vessel 2 by means of the catalyst feeding system

and metering valves 9, and by release of a suitable amount of isobutane diluent in the mixing vessel 3 through conduits 24. The amount of isobutane diluent can also be controlled using the catalyst concentration determined from the density measurement by Coriolis meter 10.

In another preferred embodiment, the method comprises diluting the catalyst slurry with hydrocarbon diluent, preferably isobutane, in the mixing vessel 3 to a concentration comprised between 0.1 and 10 % by weight. More preferably the slurry is diluted in a hydrocarbon diluent to a concentration comprised between 0.1 and 4 % by weight and more preferred between 0.1 % and 1.0 % by weight, and even more preferred of 0.5 % by weight. Preparing diluted slurry having these conc entrations advantageously enables the further use of membrane pumps 5 for injecting the slurry in the reactor 1. The use of such pumps advantageously enables to precisely and adequately control the flow of catalyst slurry injection in the reactor.

In a further preferred embodiment, the method according to the invention comprises controlling the flow rate of said catalyst slurry from the mixing vessel 3 to the polymerisation reactor 1 by determining the concentration of a reactant in said reactor 1. Prefer ably said reactant is the concentration of monomer, i.e. ethylene, in the reactor. However, it should be clear that also determination of other reactants, such as e.g. the co -monomer or hydrogen concentrations in the reactor, is comprised within the scope of the present invention. Practically, this mechanism is obtained by providing each conduit 4 for transferring and feeding the catalyst slurry from the mixing vessel 3 to the reactor 1 with a pumping means 5 that are capable of being adjusted and regulatin g the catalyst flow rate in function of the concentration of a reactant in said reactor.

In another preferred embodiment of the invention, the catalyst slurry is brought into contact with a co-catalyst. Therefore, the present invention further provides a method comprising the step of bringing a suitable amount of co -catalyst into contact with the catalyst slurry f or a suitable period of time before injecting said catalyst slurry to said reactor. The co -catalyst for the metallocene catalyst is preferably a n aluminium based compound, preferably TIBAL, as indicated herein. The co -catalyst can be supplied to the catalyst slurry either in the vessel 3, which is suitable when a relatively long pre -contact time is required between the catalyst and the co-catalyst. Preferably, the method comprises bringing a co -catalyst into contact with said catalyst slurry present in conduits 4. The co -catalyst feeding system preferably comprises a

storage vessel 11 and a conduit 12 intersecting the conduit 4, as illustrated on F IG. 1. In another preferred embodiment, the method further comprises enhancing the contact time of said co-catalyst with said catalyst slurry in the conduit, by locally enhancing the volume of said conduit 4. By locally enhancing the volume of the conduits , a better pre-contact between co-catalyst and catalyst is obtained. The present method also advantageously enables to more precisely control the ratio of catalyst/co -catalyst injection. The local enhancement of the volume is obtained by providing a contac t vessel 13 in each conduit 4. Said vessels 13 have a diameter with is considerably larger than the diameter of the conduits 4.

In another preferred embodiment, the present invention provides a method for continuously feeding catalyst slurry from the mix ing vessel 3 to the reactor 1 through conduits 4 at a suitable flow rate. The present invention provides a method that enables to continuously feeding catalyst to a reactor, without interruption of the catalyst flow.

In yet another preferred embodiment, t he invention relates to a method wherein catalyst flow rate to the reactor is accurately measured, through liquid flow rate measurement, using flow measuring means, such as preferably Coriolis flow measuring means.

While the invention has been described i n terms of presently preferred embodiment, reasonable variations and modifications are possible by those skilled in the art and such variations are within the scope of the described invention and the appended claims.

Examples

The present invention is ill ustrated by the following example of a production on a commercial - scale double loop reactor. For the comparative example a conventional catalyst feed system and control were used. The use of the current invention allows the polymerization reactor to be run at higher slurry densities with less variation than with conventional catalyst feeding control. The lower standard deviations indicate that the present invention allows for improved control of the polymerization process and thus higher product consistency .

Table 1

		Example	Comparative example
Reactor slurry density	kg/m^3	547 ± 3	531 ± 6
Ethylene flow	kg/hr	3461 ± 23	3855 ± 16
Reactor ethylene concentration	wt%	6.3 ± 0.1	6.6 ± 0.3
Catalyst slurry flow	kg/hr	70.6 ± 1.9	91.0 ± 2.8
Catalyst slurry co ncentration	wt%	0.35 ± 0.01	0.46 ± 0.05

Claims

1. Apparatus for controlling the injection of catalyst slurry in a polymerization reactor wherein polyethylene is prepared , comprising

- one or more storage vessels (2) for storing catalyst slurry consist ing of solid catalyst in a hydrocarbon diluent, whereby each vessel (2) is provided with means for transferring (6) said catalyst slurry from said storage vessels (2) to a mixing vessel (3),
- a mixing vessel (3), being connected with said storage vessels (2) by means of said transferring means (6), for diluting said catalyst slurry to a suitable concentration,
- one or more conduits (4), connecting said mixing vessel (3) to a polymerization reactor for transferring said diluted catalyst slurry from said mixin g vessel (3) to said reactor (1), whereby each conduit (4) is provided with a pumping means (5) for pumping said slurry to said reactor (1), and
- the dilution being adapted to the pumping means.

2. Apparatus according to claim 1, wherein the pumping means (5) is a membrane pump.

3. Apparatus according to claims 1 and 2, wherein the dilution being adapted to the pumping means (5) comprises a solid catalyst diluted with a hydrocarbon diluent to a concentration comprised between 0.1 and 1.5 % by weight.

4. Apparatus according to any of claims 1 -3, wherein said catalyst is a metallocene catalyst, preferably supported .

5. Apparatus according to claim 1, wherein said pumping means (5) provided on said conduit (4) is controlled in function of the concentration of a reactant in said reactor.

6. Apparatus according to any of the preceeding claims, wherein a first means (6) for transferring said catalyst slurry from a first storage vessel (2) to a mixing vessel (3) is interchangeable with a second means (7) for t ransferring said catalyst slurry from a second storage vessel (2) to a mixing vessel (3) through lines (8) connecting said first means (6) with said second means (7).

7. Apparatus according to any of the preceeding claims, wherein said means (6, 7) for transferring said catalyst slurry from a storage vessel (2) to a mixing vessel (3), each are provided with a metering valve (9), provided downstream the connecting lines (8).

8. Apparatus according to any of the preceeding claims, further comprising measur ing means (10) on said conduit for measuring catalyst flow rate.

9. Apparatus according to any of the preceeding claims, further comprising a co-catalyst feeding system, for bringing a suitable amount of co-catalyst into contact with the catalyst slurry for a suitable period of time before injecting said catalyst slurry to said reactor, said system comprising a co-catalyst storage vessel and a conduit (12) connected thereto for transferring said co-catalyst.

10. Apparatus according to claim 9, wherein sa id conduit (4) is provided with a contact vessel (13) for enhancing the contact time of said co-catalyst with said catalyst slurry in said conduit (4).

11. Method for controlling the injection of catalyst slurry in a polymerization reactor (1) wherein pol yethylene is prepared, said catalyst consisting of solid catalyst in a hydrocarbon diluent, comprising the subsequent steps of:

- providing solid catalyst and a hydrocarbon diluent in one or more storage vessels (2) such that a catalyst slurry is obtained in said vessel (2),
- transferring said catalyst slurry from said storage vessel (2) to a mixing vessel (3) wherein said catalyst slurry is diluted for obtaining a suitable concentration for use in a polymerisation reaction,
- pumping said diluted catalyst slu rry at a controlled flow rate from said mixing vessel (3) to said polymerisation reactor (1) through one or more conduits (4), by means of a pumping means (5), provided in each of said conduits (4), and
- the dilution being adapted to the pumping means.

12. Method according to claim 11, wherein said catalyst is a metallocene catalyst, preferably supported.

13. Method according to claims 11 -12, wherein said catalyst slurry is diluted with said hydrocarbon diluent in said mixing vessel (3) to a concentration comprised between 0.1 and 10 % by weight.

14. Method according to claim 11, comprising controlling the flow rate of said catalyst slurry from the mixing vessel (3) to the polymerisation reactor (1) by determining the concentration of a reactant, prefera bly ethylene, in said reactor (1).

15. Method according to claim 11 or 12, comprising transferring said catalyst slurry from said storage vessel (2) to said mixing vessel (3) at a controlled flow by controlling the ratio between diluent and catalyst in the mixing vessel (3).

16. Method according to claim 11, further comprising bringing a suitable amount of co -catalyst into contact with the catalyst slurry f or a suitable period of time before injecting said catalyst slurry to said reactor.

17. Method according to claim 16, comprising bringing a co -catalyst into contact with said catalyst slurry present in the conduit (4).

18. Method according to claim 17 comprising enhancing the contact time of said co -catalyst with said catalyst slurry in the conduit (4), by locally enhancing the volume of said conduit (4).

19. Method according to any of claims 11 to 18, comprising continuously supplying said catalyst slurry from said mixing vessel (3) to said reactor (1) through conduits (4) at a suitable flow rate.

20. Use of an apparatus according to any of claims 1 -10 for controlling the injection of metallocene catalyst slurry in a polymerization reactor wherein polyethylene is prepared

Abstract

Apparatus and method for controlling the injection of catalyst slur ry in a polymerization reactor

The present invention relates to an apparatus for controlling the injection of catalyst slurry in a polymerization reactor wherein polyethylene is prepared. The present invention also relates to a method for controlling the injection of catalyst slurry in a polymerization reactor. The apparatus and method are in particular suitable for controlling the injection of a metallocene catalyst in a polymerization reactor wherein polyethylene is prepared.

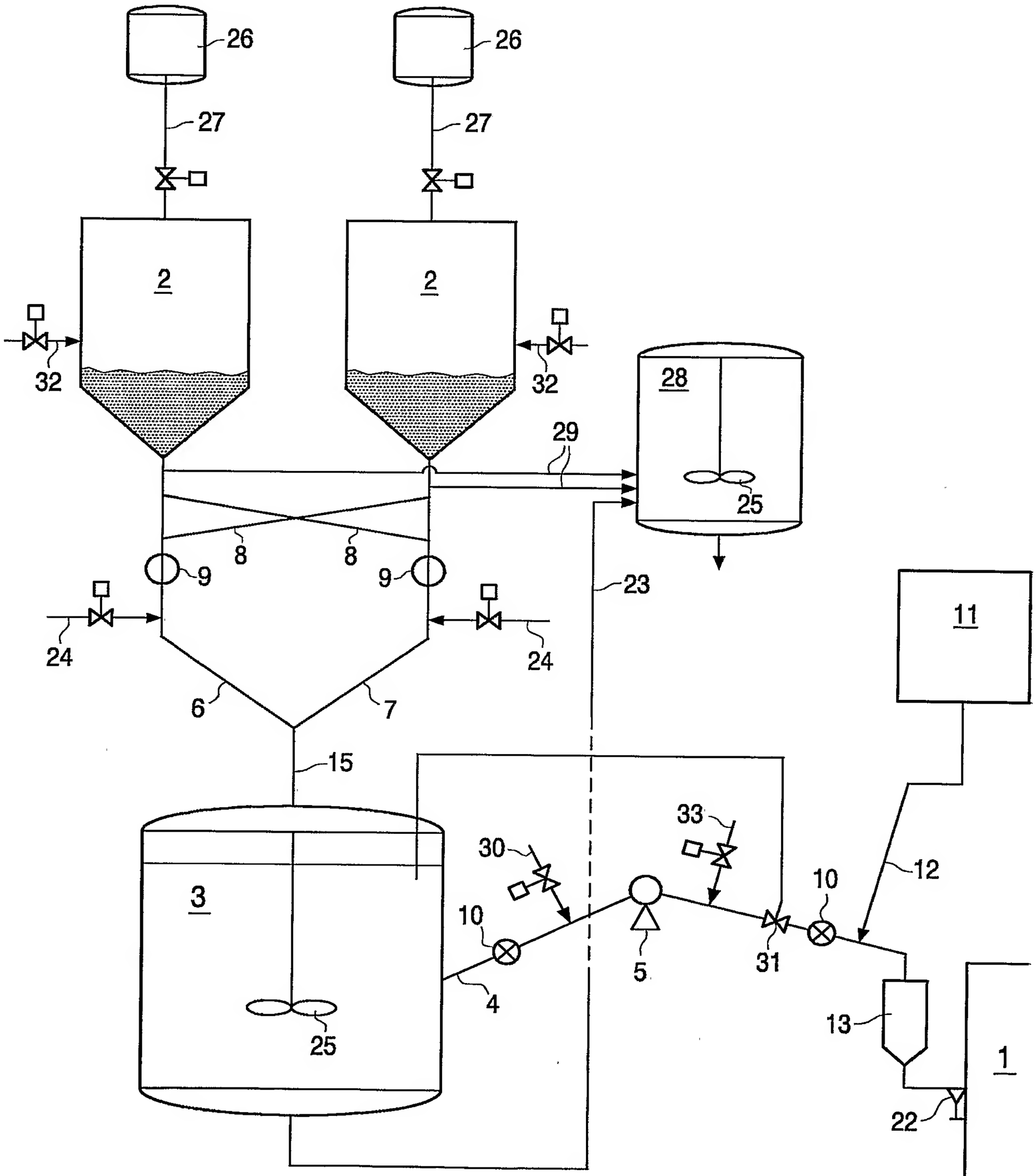
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FIG. 1

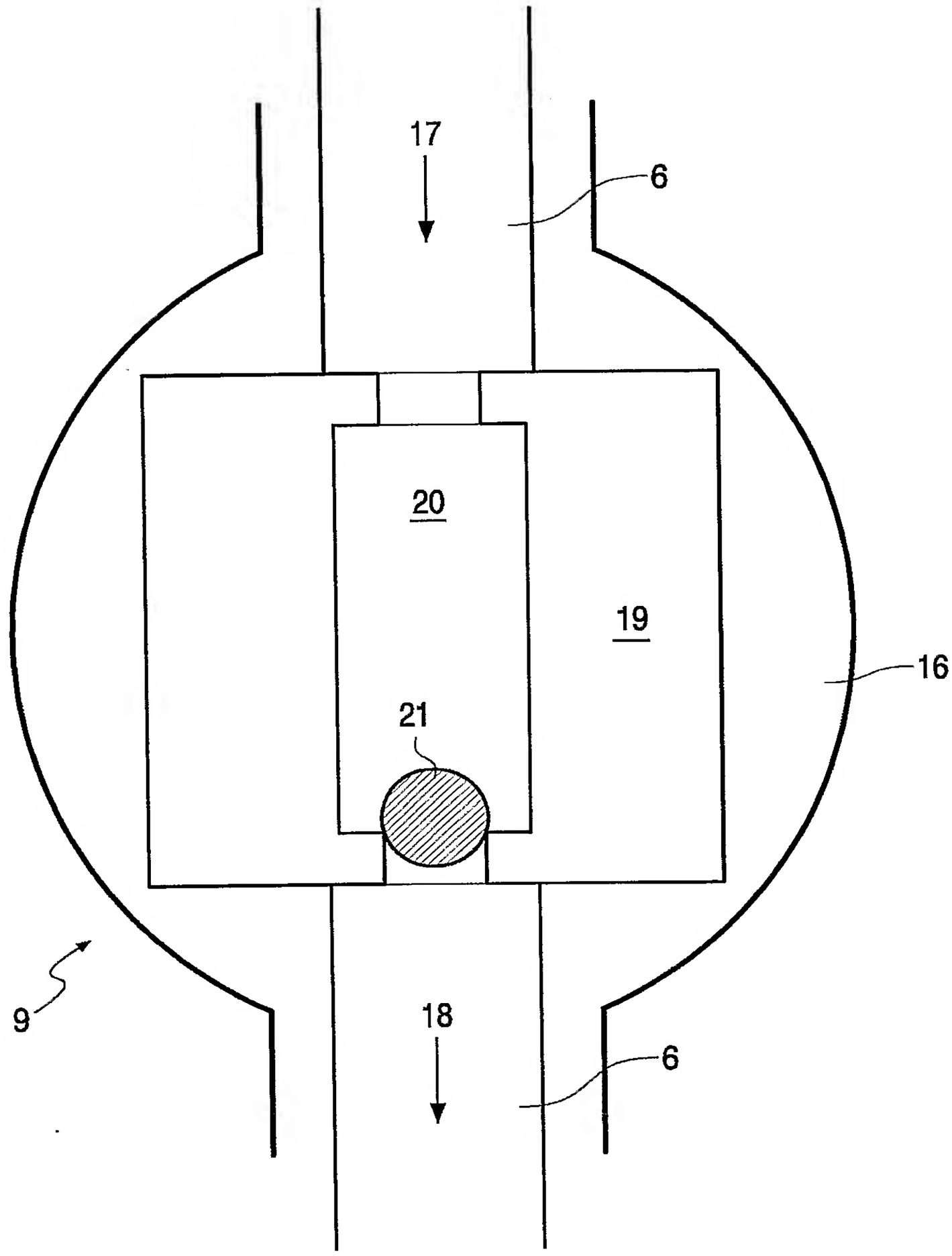

FIG. 2

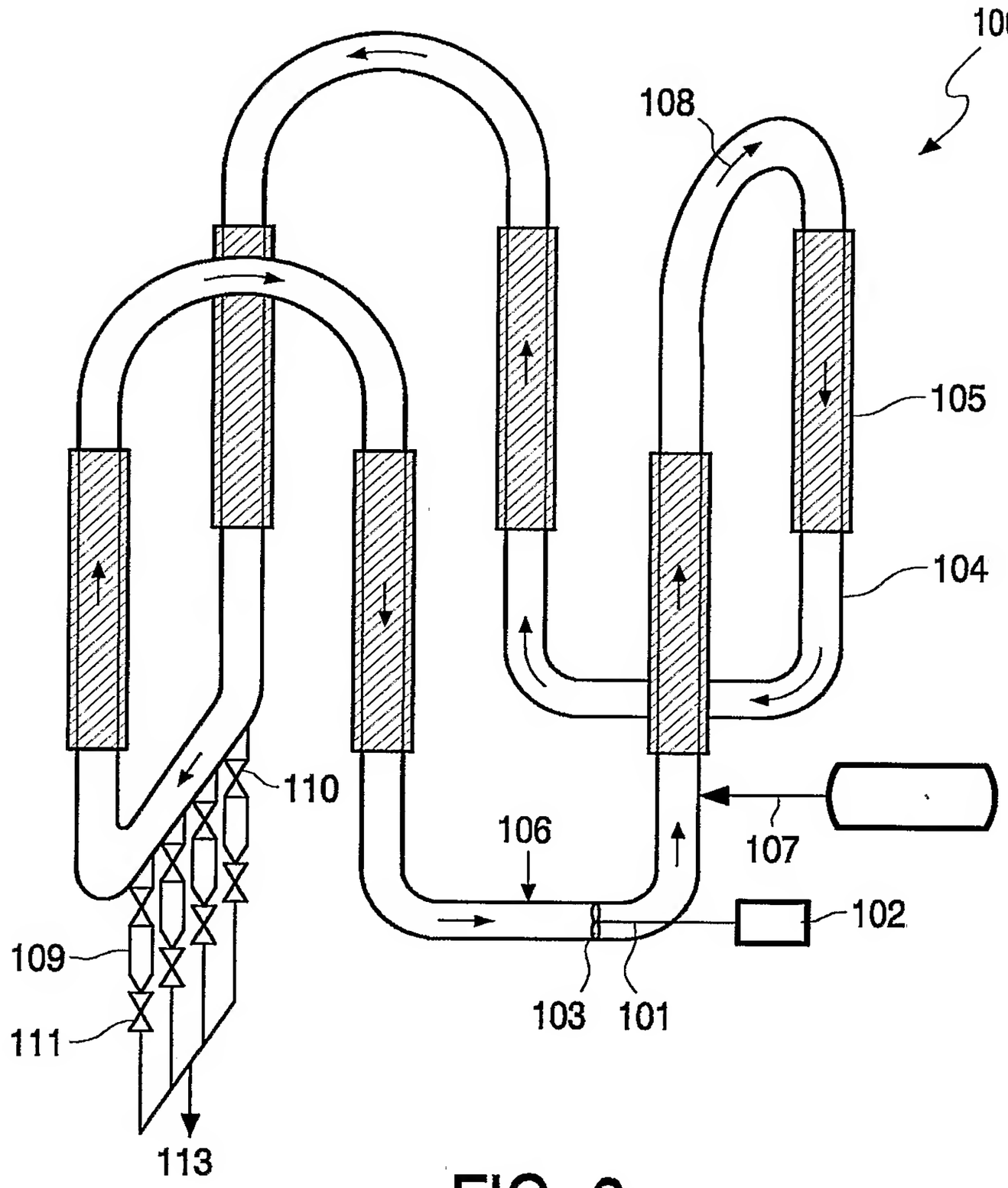

FIG. 3

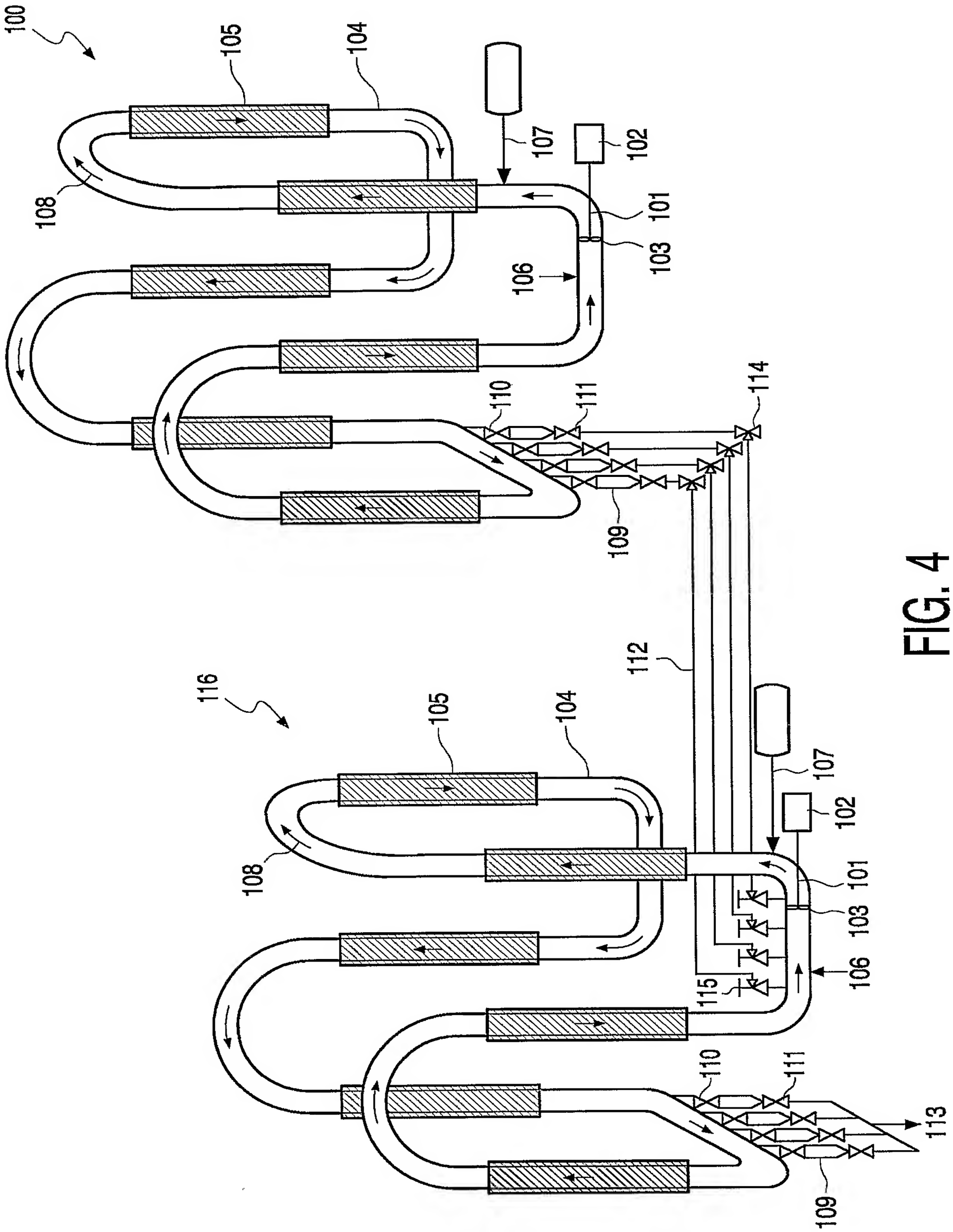
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FIG. 4